

Identification and Quantification of the Temporal and Spatial Scales of Variability in Particulate and Dissolved Material Associated with Specific Land-Use Activities in the Penobscot River System

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Contract Number: N0001404C0133

<http://www.wetlabs.com/Research/barnard/penobscotabstract.htm>

LONG-TERM GOALS

The long-term goals of this project are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions of the Penobscot River water system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

OBJECTIVES

The objectives of this project are to identify regions of defined land coverage and use activities within a watershed, investigate the biogeochemical and optical properties of the particulate and dissolved compounds that arise from each activity, identify whether those properties/compounds are unique to an activity, and thereby define observable proxies for that activity, and finally quantify the time and space scales over which the proxies are conserved. We chose the Penobscot River Watershed, Penobscot Bay and the surrounding coastal waters for four reasons. First the Penobscot River Watershed is relatively unimpacted by human activities. Second, there are distinct regions within the Penobscot watershed defined by tributary drainage boundaries that can be generally associated with distinct land use/coverage. Third, long-term climatological records for the region have indicated that precipitation has been increasing, thereby increasing the winter flow levels (Groisman et al., 2004; Keim et al., 2005; Hodgkins et al., in press). Thus there is increasing evidence that the New England region, particularly the northern section, is undergoing a climatic shift. Finally, the Penobscot Region has various existing observational programs that monitor stream discharge, meteorology, and oceanographic hydrography and optical properties. Each program has in situ infrastructure which we have supplemented with instrumentation to better determine the time and space scales of the land use tracers.

| Report Documentation Page | | | | Form Approved OMB No. 0704-0188 | |
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| Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. | | | | | |
| 1. REPORT DATE 30 SEP 2005 | | 2. REPORT TYPE | | 3. DATES COVERED 00-00-2005 to 00-00-2005 | |
| 4. TITLE AND SUBTITLE Identification and Quantification of the Temporal and Spatial Scales ff Variability in Particulate and Dissolved Material Associated with Specific Land-Use Activities in the Penobscot River System | | | | 5a. CONTRACT NUMBER | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | |
| 6. AUTHOR(S) | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) WET Labs, Inc.,620 Applegate Street, P.O. Box 518,Philomath,OR,97370 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited | | | | | |
| 13. SUPPLEMENTARY NOTES code 1 only | | | | | |
| 14. ABSTRACT The long-term goals of this project are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions of the Penobscot River water system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters). | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT Same as Report (SAR) | 18. NUMBER OF PAGES 13 | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT unclassified | b. ABSTRACT unclassified | c. THIS PAGE unclassified | | | |

APPROACH

While there are a multitude of land use activities and associated biogeochemical parameters, we are focusing on the dominant activities in Maine for which we can identify large areas of land-use activity along a stretch of river/stream in the Penobscot River Watershed. Our approach is to identify source waters that may have unique biogeochemical markers, measure those biogeochemical properties in concert with observations of the inherent optical properties of the particulate and dissolved pools, and trace the biogeochemical and optical properties from the source waters through the watershed, estuary and coastal water system. Our observational approach is two pronged: to collect water samples for biogeochemical analyses within the Penobscot River Watershed/Penobscot Bay/Eastern Maine Coastal Current System and to deploy continuous optical sensors within this system. In this way we can link our discrete biogeochemical properties to associated optical properties in order to construct a large data set of optical proxies that can be used to obtain continuous biogeochemical properties with the Penobscot System for analysis of the spatial and temporal variations in the particulate and dissolved organic loads.

WORK COMPLETED

We have been conducting approximately monthly sampling of 18 stations within the Penobscot River Watershed (Figure 1). At each station discrete water samples are collected for chemical and optical analyses: particulate organic carbon and nitrogen (POC and PON), dissolved organic carbon and nitrogen (DOC and DON), dissolved inorganic nutrients (NO_3 , PO_4 , SiO_2), fluorometric chlorophyll and pheopigments, total suspended solids and volatile solids (TSS and %VS), particle concentration and size distribution (Sequoia LISST, Agrawal and Pottsmith 2000), spectrophotometric particulate and dissolved absorption, and for selected samples, 3-d excitation/emission fluorescence (Coble 1996; Mayer et al. 1999; McKnight et al. 2001; Baker 2001; 2002a; 2002b). Additionally at each station, a WET Labs triplet sensor (chlorophyll and CDOM fluorescence and 650 nm backscattering) is deployed to obtain an in situ observation for comparison with the chemical and optical properties of the discrete water samples.

Our long-term monitoring program consists of 6 continuous stations within the Penobscot River and Upper Bay (Figure 1B and C). These sites are instrumented with WET Labs triplet sensors recording hourly observations of chlorophyll and CDOM fluorescence and 660 nm backscattering. These sites consist of three at the mouth of major tributaries, two in the main branch of the lower Penobscot River to monitor the effects of the tributary inputs and one in the upper bay that we have identified as a likely site for organic particle and dissolved matter transformation. Currently, the first of these sites was deployed last fall, three additional sites were deployed late spring of 2005, and the additional 2 sites are scheduled to be deployed in fall 2005. We also plan to deploy a combined backscattering and chlorophyll fluorescence sensor (ECO FLNTUSB) on the West Branch Penobscot River to identify the timing and intensity of cyanobacterial blooms that appear to be associated with pulp mill activities. Additionally, we plan to deploy CDOM sensors (ECO FLCDSB) at the inputs of the Mattawamkeag and Piscataquis tributaries into the Penobscot River to observe variations in the input of CDOM from a pristine wetland and an agricultural drainage basin, respectively.

We have augmented the existing 3m optical packages on GoMOOS moorings E and I (downstream and upstream of Penobscot Bay in the Eastern Maine Coastal Current, Figure 1D) with CDOM fluorometers (FLCDS) to complement the multispectral IOP and AOP packages (ac-9, vsf3,

chlorophyll fluorometers, 7-channel downwelling irradiance and upwelling radiance). We have also instrumented mooring F in the Penobscot Bay with a WET Labs ECO sensor to monitor chlorophyll and CDOM fluorescence and NTU scattering sensor as well as 7-channel incident irradiance and upwelling irradiance.

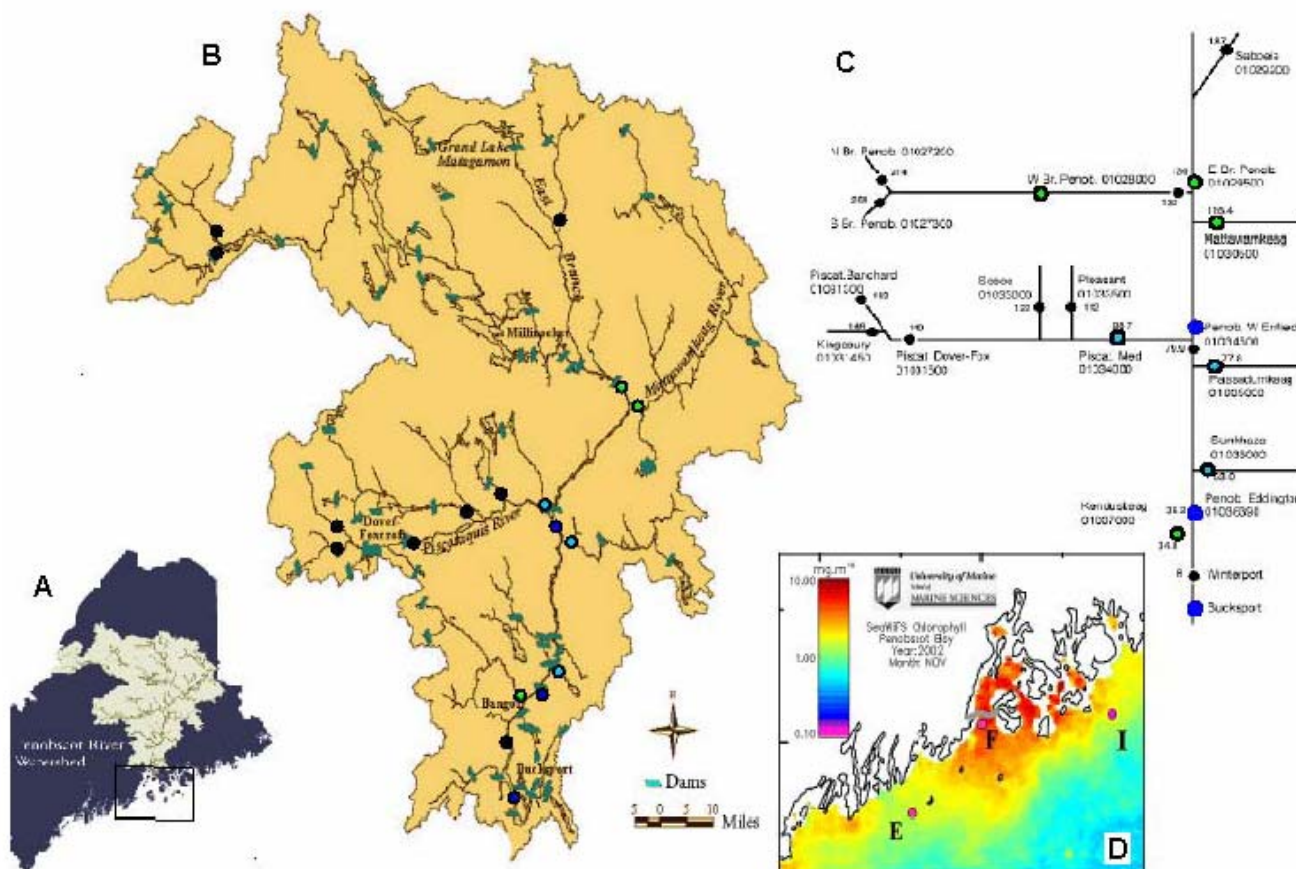


Figure 1. A. Map of the state of Maine showing the extent of the Penobscot River watershed and the tributaries. B. Detail of the watershed and tributaries of the main drainage basins with the sampling stations (symbols) and continuous triplet (blue and cyan) and short cycle FLNTU and FLCDS (green) monitoring sites. C. Site schematic of the sampling and monitoring stations showing the distance (km) relationship between the stations relative to Bucksport. Eight-digit numbers indicate USGS station name. From T. Huntington, USGS. D. False color SeaWiFS chlorophyll image of Penobscot Bay and the coastal waters of the Eastern Maine Coastal Current showing the location of GoMOOS moorings E, F and I.

RESULTS

Our primary in situ optical parameters are chlorophyll fluorescence, CDOM fluorescence and particle scattering. These are direct proxies for chlorophyll concentration, CDOM absorption and total suspended particle mass (e.g. Bishop 1986; Vodacek et al. 1997). Optical proxies are developed based upon relationships between discrete in situ optical properties measured with a WET Labs triplet sensor and associated water sample analyses of the particulate and dissolved matter. Beyond the order one relationships we are developing carbon-based proxies: algal carbon, dissolved organic carbon and

particulate organic carbon, respectively (e.g. Bishop 1999). Ancillary optical observations (spectral slope of dissolved absorption, partitioned particulate absorption, 3d-ExEm dissolved fluorescence), particle size distribution, and biogeochemical properties (carbon to nitrogen ratios of the particulate and dissolved components) are being used to derive optical proxy relationships to discern particle composition and size distribution and dissolved matter composition. Initial results indicate that the dissolved component composition varies significantly as a function of land use as does its optical properties, particularly with regards to agricultural versus wetland coverage (and those two are the most significant contributors to DOC in the river). The organic to inorganic particle ratio as well as the algal to non-algal particle ratios also appear to vary with land coverage, particularly during high flow periods when particles remain suspended in the water column. Currently our optical proxy analyses encompass July 2004 through August 2005 and are anticipated to continue under the current program until December 2005.

Chlorophyll concentrations in the watershed were generally less than $2 \mu\text{g l}^{-1}$. The in situ-estimated concentrations were found to be generally less than $3 \mu\text{g l}^{-1}$ and thus within the established range of variation (Figure 2). Two sets of outliers are apparent, the first occurred in the July 2004 sampling of the West and main branches of the Penobscot during a cyanobacterial bloom in Dolby Pond, near Millinocket, Maine. This bloom appears to have occurred in response to an uncontrolled release of phosphorous from the local pulp mill. The algal concentrations in Dolby Pond exceeded $100 \mu\text{g l}^{-1}$ at its peak, and at the time of the triplet sampling were above $10 \mu\text{g l}^{-1}$ at the downstream sampling site on the West Branch. Concentrations down the main branch were also enhanced but the enhanced chlorophyll concentrations were not detected by the in situ fluorometer because the cyanobacterial accessory pigments were not stimulated by the LED. The second exception yielded higher fluorescence relative to chlorophyll due to exceptionally high concentrations of fluorescent CDOM in the Sunkhaze Creek which bled into the chlorophyll fluorescence channel. Ignoring the two exceptions, the calibrated in situ fluorometer provides robust estimates of chlorophyll within the limitations of the methodology.

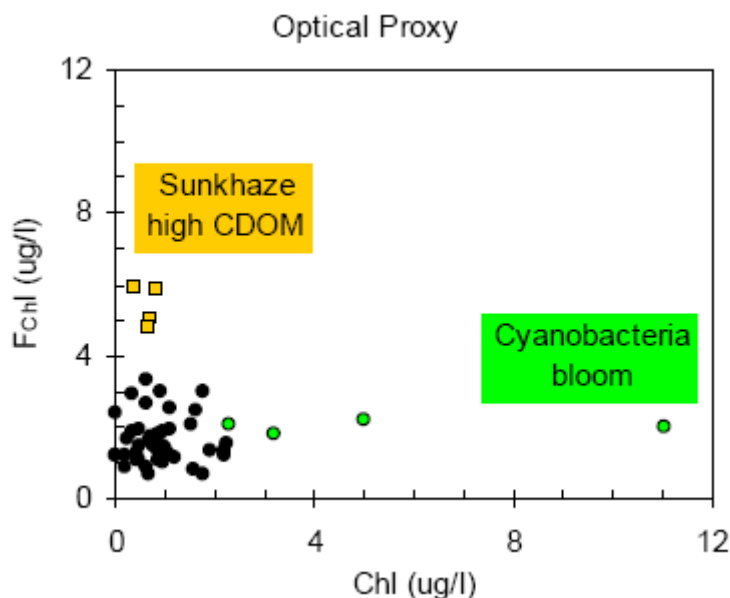


Figure 2. Relationship between calibrated in situ chlorophyll fluorescence measured with the triplet and extracted chlorophyll a concentration for samples collected July and October 2004 and May and August 2005. Green symbols indicate samples associated with a cyanobacterial bloom and waters downstream from the source. The bloom was identified by microscopy and spectrophotometric absorption. Yellow symbols indicate the samples collected in Sunkhaze Creek which is characterized by very high concentrations of fluorescent CDOM the signal of which contaminated the in situ chlorophyll fluorometer.

Particulate matter concentration is quantified using total suspended solid analyses (TSS, mg/l; EPA 1979). The observed range was 0.01 to 25 mg l⁻¹, with values >3 mg l⁻¹ observed during time of the largest discharge in the spring at nearly all stations and throughout the year at those stations impacted by marine waters. Particulate organic carbon concentrations ranged from approximately 30 to 850 µg l⁻¹. To first order, the total particle backscattering is related to the total particle concentration, with second order dependence on particle size distribution and composition. Excluding the marine samples, the backscattering coefficient varied 10 fold from 0.001 to 0.012 m⁻¹, although most of the values were <0.005 m⁻¹, with no discernable relationship to TSS (Figure 3), except for those samples collected in October 2004, for which a statistically significant correlation was found ($r^2 = 0.69$, $n=14$). While less significant, the relationship observed in May 2005 was statistically similar (i.e. same slope) although the deviations about the line were larger. No relationship was observed in August 2005. As far as subwatershed characteristics, only the Kenduskeag and Passadumkeag tributaries demonstrated characteristics different from the mean. Both had the highest b_b coefficients and TSS concentrations, although not sufficient to be resolved downstream in the main branch of the Penobscot River with the current data set. The single largest factor in particle concentrations was discharge, indicating that the particulate matter in the system appears to be physically driven and less a function of watershed characteristics. Furthermore this would indicate that variations in particle size distribution, as a function of resuspension forces, may be a large source of the observed variability in the backscattering and TSS relationship (Walling and Moorehead 1987).

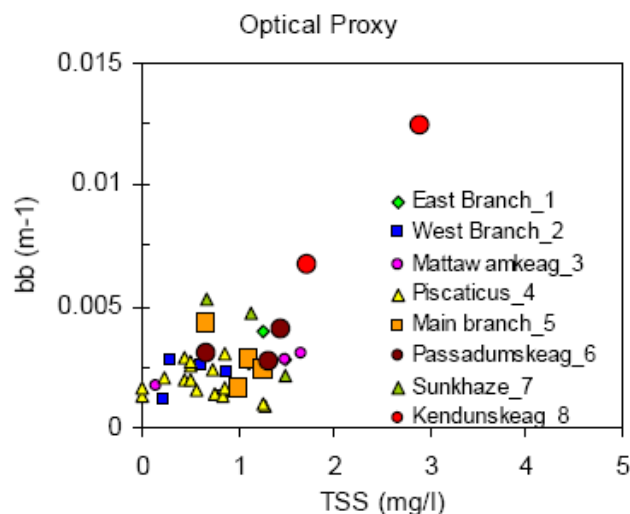


Figure 3. Relationship between particle backscattering coefficient (660nm) and total suspended solids (mg l^{-1}). Symbols indicate the 7 subwatersheds and main branch of the Penobscot River (see Figure 1). Enlarged symbols indicate those subwatersheds and the downstream main branch stations for which a significant relationship was observed. No seasonal pattern was observed.

The relationship between backscattering and POC is highly variable between sampling times (Figure 4) indicating significant variations in the particle composition. The three highest backscattering data points are all associated with marine waters (Winterport) and in one case the Kenduskeag in October. The most organic rich particles were found in July, followed by the October samples, with the least organic particulate matter found in May. This is expected as the May sampling was associated with the strongest precipitation and ice melt discharge which would induce the greatest sediment resuspension and transport, followed by the fall precipitation discharge with minimal discharge in July.

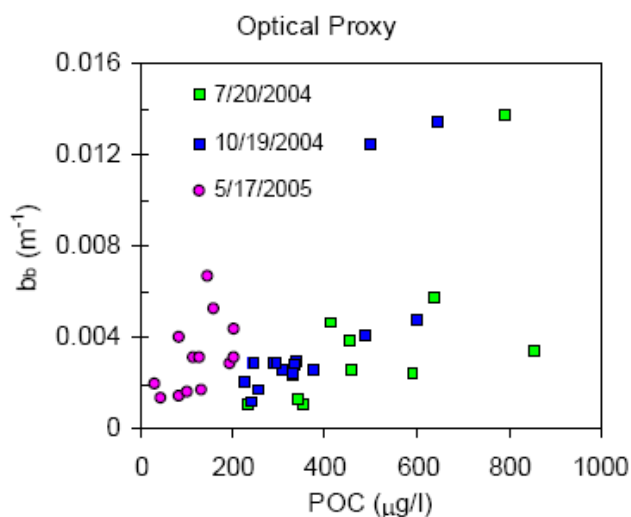


Figure 4. Relationship between total particle backscattering and the POC concentration as a function of sampling date.

Particulate matter composition can be chemically defined using the molar ratio of organic carbon to nitrogen, with lower values (~7-10) being indicative of algae and other primary producers and higher values indicative of higher trophic organism and detritus. Observed values ranged from 5 to 18 with median values of 11; lowest values were observed in the spring and during a summer phytoplankton bloom, highest values in October (Figure 5). The compositional proxy of particle backscattering to chlorophyll fluorescence should provide an indication of the total particles that are algal and thus should be related to the C:N ratio if the particle load is dominated by organic rather than inorganic particles. This was found to be true only for the Kenduskeag and those stations downstream in the main branch of the Penobscot (Figure 5), otherwise the optical ratio was found to be relatively invariant while the C:N ratio varied over its whole range.

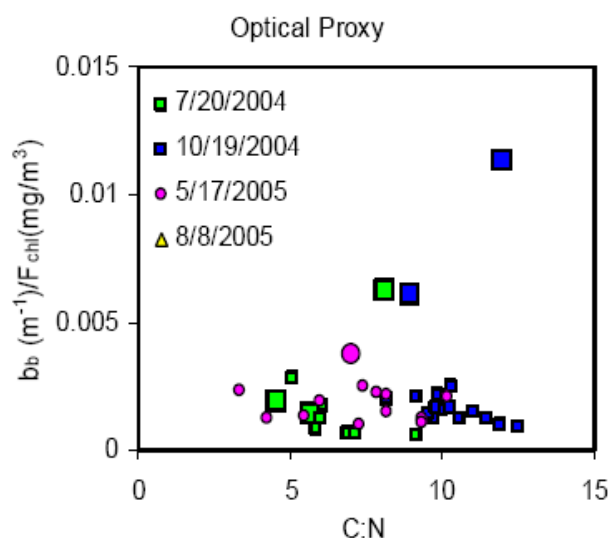


Figure 5. Optical and chemical proxies for particle composition: backscattering to chlorophyll fluorescence and organic carbon to nitrogen for three sampling dates. Enlarged symbols are for the Kenduskeag subwatershed and the downstream stations in the main branch.

Colored dissolved organic matter concentration (CDOM) is estimated by the magnitude of the absorption coefficient of the dissolved fraction, a_{CDOM} , (Blough et al. 1993) with the assumption that there is a relationship between the colored and non-colored fractions of dissolved matter. Similarly, the magnitude of the fluorescence is also used as a proxy for DOM concentration, although the fraction of fluorescing dissolved matter is smaller than the absorbing fraction. One chemical description of DOM concentration is the dissolved organic carbon concentration, DOC, a robust estimator as carbon is the primary component in the DOM pool. The relationship between the two optical proxies is approximately linear for samples with absorption $<30 \text{ m}^{-1}$ at 370 nm (Figure 6). The only samples above that value are those collected from tributaries that drain freshwater wetlands and bogs. The relationship between the in situ fluorescence and DOC is more strongly linear than the absorption-fluorescence relationship (Figure 7). The samples are statistically grouped by subwatershed with no apparent dependence on the sampling timing (May, July, October). The lowest concentrations are found in the agriculturally-dominated Piscataquis and timber/lumbering-dominated West Branch subwatersheds. The highest concentrations are found in the wetland dominated watersheds. The differences between subwatersheds and land coverage type are statistically significant.

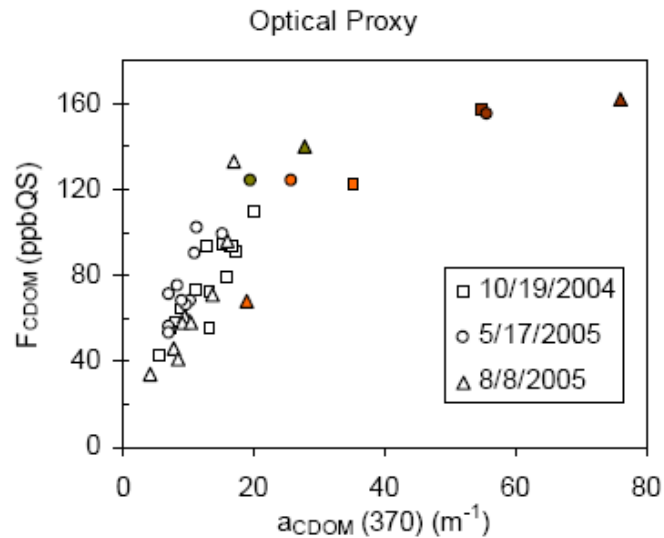


Figure 6. Relationship between in situ CDOM fluorescence and spectrophotometric absorption at the fluorescence excitation wavelength (370nm) for three sampling dates. Colored symbols indicate those collected from the three tributaries draining wetland dominated subwatersheds (Sunkhaze – dark brown, Passadumkeag –light brown, and Mattawamkeag –olive).

The spectral slope of the CDOM absorption coefficient has been shown to be sensitive to the composition of the CDOM (Carder et al. 1989; Simeon et al. 2004) with steeper spectral slopes associated with refractory fulvic matter and flatter spectral slopes associated with more labile humic matter. The steepest slopes are consistently found in the late summer low flow season relative to the May and October sampling times (Figure 8). The wetland sites with the highest CDOM absorption are also characterized by the flatter slopes (more labile material) although within each site, the steepest slope was found during the August sampling. The steepest slopes were consistently found in the Piscataquis subwatershed. These observations suggest that there are significant compositional differences between wetland sites and non-wetland sites but that transformations occur at all sites during the summer which transform the composition of CDOM at all sites to that more similar to wetland CDOM. Based upon the data collected thus far, the CDOM component exhibits the strongest optical/biogeochemical proxies and the most distinct properties as a function of subwatershed coverage, both concentration and composition. Additionally dissolved matter properties were not correlated with river discharge

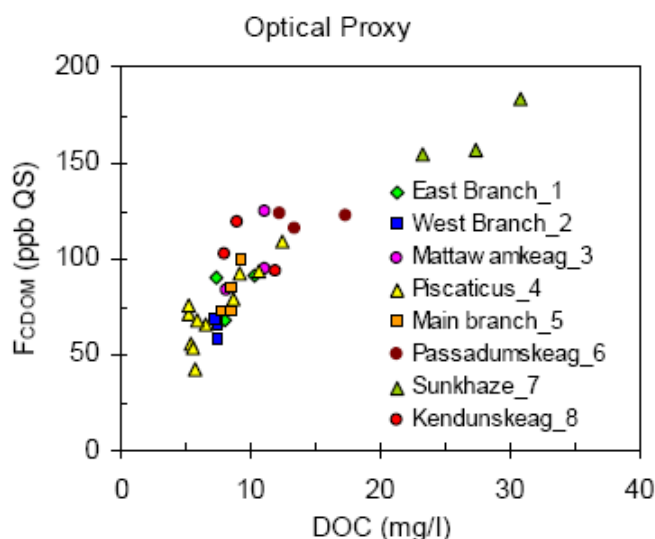


Figure 7. Relationship between in situ CDOM fluorescence and DOC (analyzed by Dr. George Aiken, USGS, Boulder, CO) as a function of subwatershed. The linear relationship has an $r^2 = 0.86$.

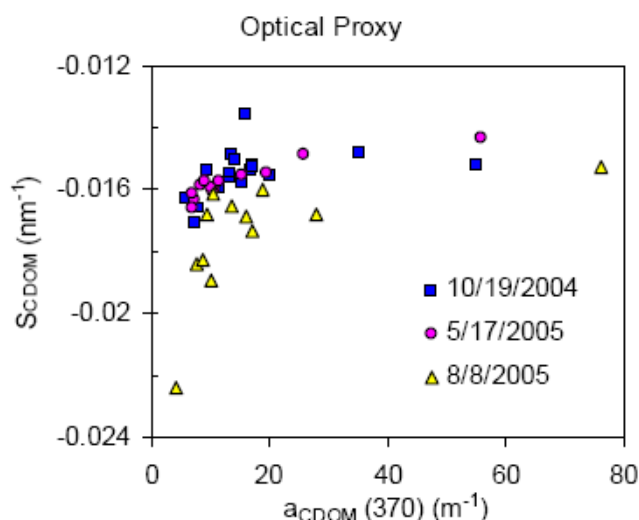


Figure 8. Relationship between the spectral slope of CDOM absorption and the magnitude of CDOM absorption (370 nm) as a function of sampling date.

The primary purpose of the time series of the moored triplet sensors within the Penobscot River/Bay system is to provide the temporal context for interpreting the delivery and transport of these materials. Data collected during the late spring and summer of 2005 correlate well with the above optical proxy analyses (Figure 9). Similar patterns in chlorophyll and cDOM fluorescence, elevated levels in late spring and gradual decline through summer, indicate that both parameters are to first order controlled by large scale synoptic events (volume discharge and solar insolation). The Passadumkeag River is clearly a large source of both chlorophyll and cDOM to the Penobscot River. In terms of suspended solids, the low and relatively consistent levels of backscattering observed indicate that the system appears to be much more physically driven. Results from the July through April observations have

suggested that there are significant and traceable differences in the amount and composition of materials entering the Penobscot River via tributary drainage basins and that this material undergoes transformations in the upper portion of Penobscot Bay. Our working hypothesis is that during high flow periods, the material transport rate exceeds the transformation rate and that we can observe clear land use/coverage signals within Penobscot Bay and the coastal waters. However, during low flow periods, transformation exceeds transport and these signals may be degraded within the Bay. A survey conducted in early June 2005 of the lower Penobscot River and Bay using the ferry system showed an inverse relationship between salinity and the absorption coefficient at 425 nm as expected (Twardowski and Donaghay 2001), indicating that as the river water enters the Penobscot Bay, both physical mixing with the oceanic end member and transformation of the high cDOM material are likely to be occurring. The spatial patterns resolved from this survey also indicate that these processes are occurring through the western branch of the Bay (Figure 10).

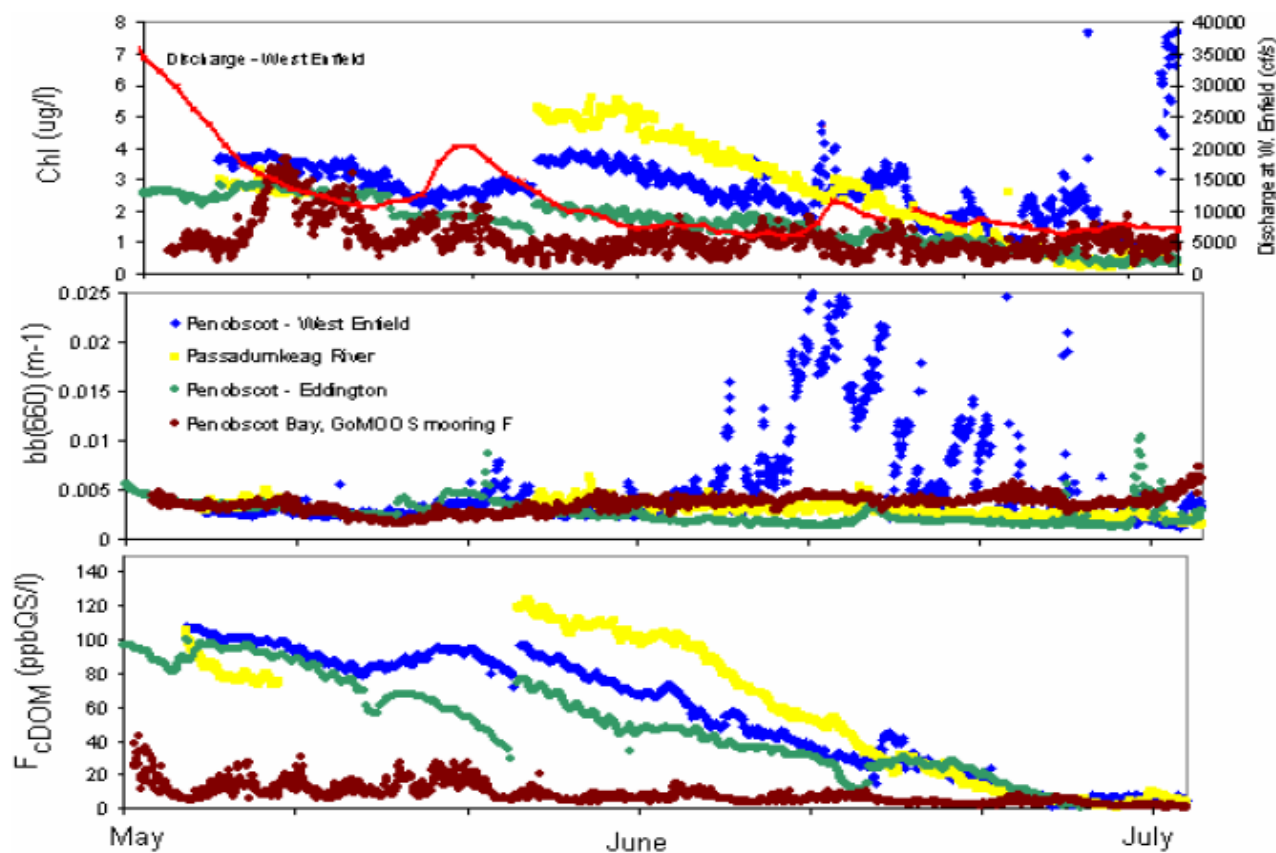


Figure 9. Time series of optical parameters (top, calibrated chlorophyll fluorescence, middle, backscattering coefficient, bottom, calibrated CDOM fluorescence) collected at three sites within the Penobscot River system using the moored ECO triplet sensors for late spring to early summer 2005. Also shown is the time series of the same parameter collected from the GoMOOS mooring F located at the mouth of Penobscot Bay. The calibrated discharge at West Enfield gage site is shown in the top panel.

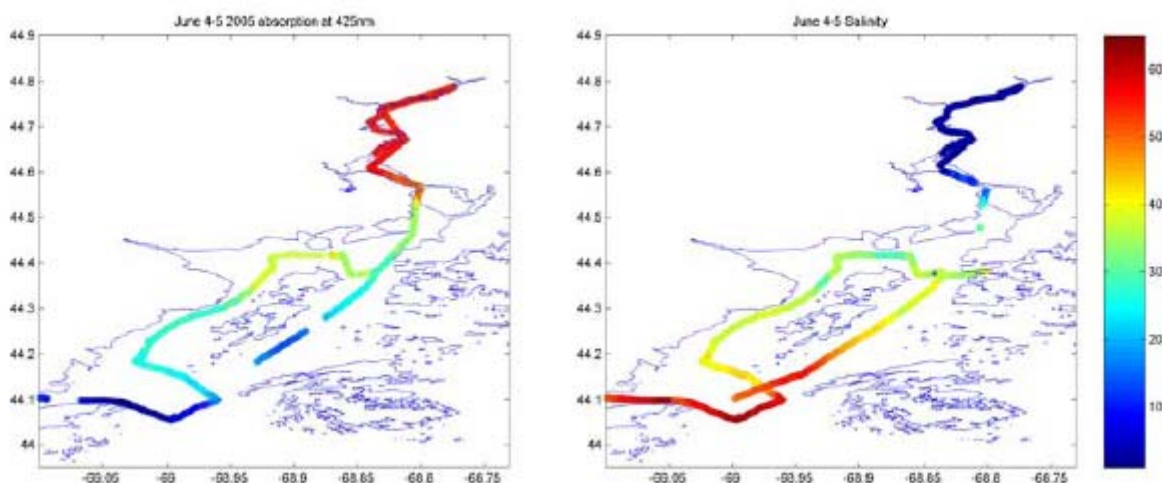


Figure 10 – Spatial distributions of the absorption coefficient at 425 nm and salinity at the surface on June 4-5, 2005, measured using the inline ferry system. The absorption ranges from 0.92 m^{-1} (dark blue) to 9.16 m^{-1} (dark red), and the salinity from 0 (dark blue) to 29.86 PSU (dark red).

IMPACT/APPLICATIONS

The results of this study will contribute to identification of optical and biogeochemical signatures associated with specific land use activities, and quantification of the tracer potential of those signatures through the river and estuarine system to the coastal environment. The application of this approach is the capability for determining changes in terrestrial land use from autonomous observations in the river and coastal waters. Identifying the conservative and nonconservative optical and chemical variability in the dissolved and particulate fractions of river inputs will also contribute to the development of coastal and watershed models of carbon flux. The high temporal resolution data obtained in this study will allow for quantification of this variability on time scales of hours to months, covering a range of scales from daily to seasonal to interannual and including episodic events. While the focus of this study does not address the specific transformations operating within a riverine impacted regions, these results will be useful in aiding our understanding of the relevant biogeochemical processes operating in the coastal margins influenced by riverine inputs by determining the appropriate temporal and spatial scales of optical and chemical variability that are conserved through the system.

TRANSITIONS

The USGS Augusta, ME office has shown a strong interest in transitioning the ECO triplet river observation systems we will be deploying in the Penobscot River. We will be testing these systems on a long term basis in the spring of next year and will provide results and reports on the operational performance of these systems to the USGS for their review.

RELATED PROJECTS

1. Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions.
2. The Gulf of Maine Ocean Observing System (GoMOOS), which Dr. Roesler is funded by to maintain optical instrumentation and data streams from the mooring observation program, is providing valuable hourly time series of coastal optical and physical surface properties upstream and downstream of the Penobscot River. Beginning in the fall of 2004, optical sensors (backscattering, chlorophyll and cDOM fluorometers) were installed on a GoMOOS mooring in the center of the mouth of the western branch of Penobscot Bay. Data from these systems are providing a wealth of information as to the hourly to seasonal variability in the dissolved and particulate materials within the river to coastal transition zone of the Penobscot Bay.

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